THE EFFECT OF BIOMASS ON FIRECRACKERS FORMULATION: AN EXPERIMENTAL STUDY

A SYNOPSIS

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1. INTRODUCTION

Fireworks are widely used in all cultures, religious and social occasions for crowd-pleasing throughout the world. Firework industries are one of the major revenue sources for the Indian government and the town, Sivakasi in India is the place which contributes to 90% of the production of firecrackers. Firecrackers are available in different variety namely sparklers, chakker (rotating type), bijili cracker, chorsa (garland type cracker made from bijili), atom/cracker bomb, rocket, color fountain, and aerial fireworks (fancy type). Among the aforementioned firecrackers, bijili is one of the highest sold items in the recent past in firecrackers types. Chorsa (garland of bijilis) is made of with the minimum hundred numbers of bijilis and maximum with ten thousand bijili. The flash powder chemical composition of bijili crackers is 60% of potassium nitrate (KNO_3), 20% of Aluminum (Al) and 20% of Sulfur (S). This same percentage of flash powder composition is used for making other types of crackers by varying its mass depending upon the noise level. In the flash powder composition, Al acts as fuel, S as an ignition source and KNO_3 act as oxidizer which supplies the oxygen needed for burning. All these chemicals are used in a powdered form for making flash powder. The particle size of the fire cracker chemical ingredients are in the range of 50 nm and cashew nut shell powder is 43µm. Grinding of powders, sieving to the desired size, mixing the powder to obtain a homogenous chemical mixture and packing them in the paper container are the steps followed for making the bijili crackers. There are a lot of options to improve the performance of flash powders like changing their composition of the fire cracker, addition of new chemicals in fire cracker chemical mixture, and reducing the particle sizes of the chemical ingredients. Burning of fireworks releases gases like SO_2, NO_x and CO_x, suspended particles which causes to pollute the environment as well as create serious health hazards to the human being. The permissible limits of SO_2 given by Central Pollution Control Board (CPCB), India and World Health Standards was exceeded during the Diwali festival season.

The sulfur powder in flash powders chemical mixture is highly sensitive (Melting point: 112ºC) and minor mistakes of the worker in their workplace create workplace hazards. The chemical composition and its quantity of the flash powder is carefully chosen to avoid fire hazards. The research works done for analyse the thermal stability and cracker characteristics of cracker chemical mixture and using of nano scale

of chemical mixture. The utilization of bio mass in fire cracker application is not discussed in research paper. The objective of this study is to utilizing of bio mass like Tamarind Seed Powder and Cashew Nut Shell powder by reducing the amount of sulfur without comprising the noise and safety performance of normal fire cracker.

2. LITERATURE REVIEW

Literature survey was done on the fire cracker manufacturing process, occupational hazards and human health issues, environment pollution and its effects, accidents data, accident causes and its effects. The application of bio mass in fire cracker also discussed.

The manufacturing process of firecrackers involves starting from taking the chemical powders, weighing, mixing, filling, drying, fuse making, fuse cutting, fuse inserting, and finally packing [1-2]. The firecracker is prepared as per standard procedure followed in fireworks industries and the dimensions of the container fixed based on the PESO standard [3].

There are more accidents are occurred in fireworks industry during involved in various processes of making a cracker like mixing of chemical powders, filling of chemical powders, storage of chemical powders and cracker and transportation of fire crackers [4]. During mixing of chemical powders there are more accidents are occurred due to friction, impact, static electricity, unsafe acts like human error and, unsafe conditions [5]. The major hazards concerned in firework industries are toxic gas release like SO_2 during bursting, fire and explosion occurred during handling of chemical mixtures due to irregular chemical composition and its quantity [6].

According to Petroleum Safety and Explosive Organization (PESO) firework accident data report 2010-11 to 2018-19, 28% accidents occurred due to friction, 16% impact, 15% carelessness of the workers, 5% lightning, using of irons and using of electrical appliances, 17% thermal decomposition, 7% mishandling and 2% static electricity [7]. All the aforementioned accident causes by irrespective of the chemical mixture and its quantity. So the chemical composition and quantity of chemical mixture is carefully chosen to avoid accidents. The fireworks employees suffered from severe burns with inhalation injury and associated injuries that led to high mortality [8].

The burning of fireworks products releases contaminated particles like SO_2, CO_2, CO, suspended particles, and several metals like aluminium, magnesium, and manganese which are allied with serious health hazards [9].

The emission rate can be controlled by utilizing bio mass like Tamarind Seed Powder and Cashew Nut Shell Powder in fire cracker mixture. Tamarind Seed Powder and Cashew Nut Shell Powder can be used as a fuel because of its combustion property and also its calorific value of 21 MJ/Kg and 20 to 22MJ/Kg. Tamarind Seed Powder contains high value of weight percentage of carbon (47.76 %) and oxygen (42.39 %). Similarly Cashew Nut Shell Powder consists of Carbon (45.21%), Oxygen (37- 47%) and Moisture content (6-10%) [10-19].These bio masses helps to balance the sulfur role in normal mixture during the chemical reaction when bursting of fire cracker and maintain the performance as optimum level.

Tamarind seed is a solid waste [20] and the weight of tamarind seed is concerning 40-44% of tamarind fruit and it is widely grown in India with an annual growth of about 300,000 tons [21]. The tamarind seeds and cashew nut shell were kept at oven and dried at 110 °C for 12 h period to remove moisture content [10] and crushed to fine particle and powder form is produced.

The flash powder chemical composition is prepared and the fabrication of fire cracker is followed by standard procedure prescribed in Petroleum and Explosive Safety Organization PESO [3]. During reduction of sulfur in fire cracker chemical mixture consider the cracking behaviour of the fire cracker. The sulfur range should be 10% to 17% in flash powder chemical mixture is necessary to impart good cracking characteristics for flash powders chemical composition which is used for making fire crackers [22].

The limiting impact energy of the chemical mixture is measured as per the standard procedure described by German Federal Institute for Testing Materials, Bundesanstalt für Materialforschung und –prüfung (BAM)-UN Test Series.3 [23,24]. Similarly the friction sensitivity of the chemical mixture was experimentally tested using BAM friction sensitivity test apparatus and the procedure for measurement is described [25].

Noise level test was carried out as per the rules and notification specified by Petroleum and Explosives Safety Organization, Govt. of India. It was measured by

noise level monitors using Model no.824L (Make: Larson and Davis, USA) and the measurement procedures are discussed [26]. The noise level produced by crackers at a distance of 4 m from the point of bursting is recorded in dB (AI) and dB (C) values [27, 28].

3. OBJECTIVE

- The objective of this research work is to reduce the emission rate of SO2 by fabricating eco-friendly fire cracker.
- To optimize the performance of the fire crackers by comparing normal with modified fire crackers chemical mixture.
- The cracking behaviour and performance of the modified fire cracker are retained when changing the chemical composition of the normal fire cracker.

4. RESEARCH PROBLEM

From the thorough literature survey, the following research gaps is determined.

- The utilization of Biomass like Tamarind Seed Powder and Cashew Nut Shell Powder in firecracker industry is not discussed.
- Research works done to analyzing the thermal stability, cracker characteristics, and sensitivity analysis of the cracker chemical mixture using nano scale.
- Research work was done only for changing the chemical proportion of the firecracker chemical mixture.
- Research works done for replacing sulfur powder by adding fructose to cracker mixture for aerial fireworks. The reduction of sulfur by adding TSP & CNSP in sound emitting fire cracker is not reported.

5. ORGANIZATION OF THESIS

Chapter 1: Introduction

In this chapter discussed about introduction of fireworks industry, fire cracker Chemical composition, and effect of chemical powders and fabrication process of fire cracker. The types of sound emitting fire crackers, normal and bio mass based fire cracker raw materials are provided. The hazards are involved in various manufacturing process of fire cracker is discussed. The

international safety standards applicable for fireworks industries were also discussed.

Chapter 2: Literature Review

A detailed literature survey provided on the recent research regarding various issues including human health issues, environment pollution, environmental effects caused by bursting of crackers, fireworks accidents like fatalities and non-fatalities data, root causes of accidents. Further this chapter discussed about the effects of irregular chemical composition and its ratio. The standard procedure for conducting experimental setup as per PESO and BAM test method are discussed. The utilization of bio masses like Tamarind Seed Powder and Cashew Nut Shell Powder background in fire cracker applications are also discussed well. Based on the literature review, it presented the research gap in this area. The objectives of this research work have been articulated as well.

Chapter 3: Materials and Experimental details

This chapter provides the research methodology used for this research work in Figure 1.The chemical ingredients used for making normal and Bio mass like Tamarind Seed Powder and Cashew Nut Shell Powder based fire cracker is discussed. It also provides the detailed procedure for the experimental setup like Nosie Level Test Frictional Sensitivity test, Impact Sensitivity Test, and Emission test. This chapter also discussed about the Thermal analysis such as Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) of the normal and Bio mass based fire cracker.

Chapter 4: Characterization of chemical ingredients

This chapter describes the characterization studies of Tamarind Seed Powder and Cashew Nut Shell Powder such as Fourier Transform Infra-Red spectroscopy (FTIR), Particle size analysis (PSA) and Morphology analysis (SEM).

4.1 FTIR

FTIR test will give the presence of exact molecular structure and the functional groups of the Tamarind Seed Powder and Cashew Nut Shell Powder organic compounds.

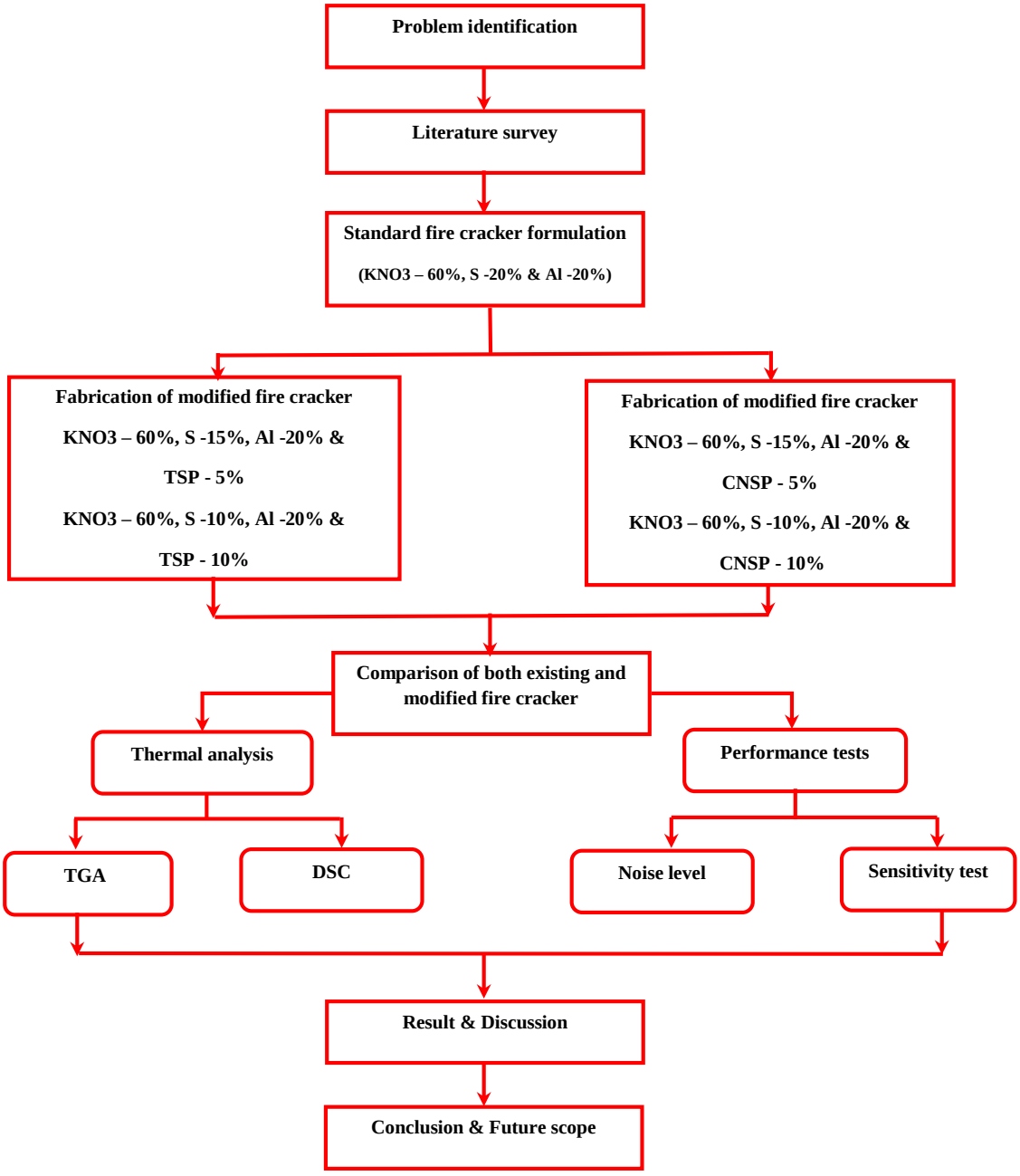
Problem identification
Literature survey
Standard fire cracker formulation
(KNO3 – 60%, S -20% & Al -20%)
Fabrication of modified fire cracker
KNO3 – 60%, S -15%, Al -20% &
TSP - 5%
KNO3 – 60%, S -10%, Al -20% &
TSP - 10%
Fabrication of modified fire cracker
KNO3 – 60%, S -15%, Al -20% &
CNSP - 5%
KNO3 – 60%, S -10%, Al -20% &
CNSP - 10%
Comparison of both existing and modified fire cracker
Thermal analysis
Performance tests
TGA
DSC
Noise level
Sensitivity test
Result & Discussion
Conclusion & Future scope

Figure 1 Research Methodology

4.2 PSA

The particle size distribution of all the raw materials used for making fire cracker like Potassium Nitrate, Sulfur, Aluminium Tamarind Seed Powder and Cashew Nut Shell Powder were observed and it is one of the important parameters in firework industries regarding safety aspects. The average particle size of all the raw materials used for making fire cracker was 0.05 μm (50 nm)

4.3 SEM

The morphology of the flash powder sample was observed through JSM-7900F Schottky Field Emission Scanning Electron Microscope. The average particle size (43 μm) of CNSP and also the average particle size of all other raw materials like Potassium Nitrate, Sulfur, Aluminium, and Tamarind Seed Powder was 50nm confirmed from the distribution plot.

Chapter 5: Effect of Tamarind Seed Powder Based Fire Cracker for making Eco-Friendly Cracker

This chapter includes effect of normal fire cracker and Tamarind Seed Powder based fire cracker on noise level performance, sensitivity analysis like friction sensitivity, impact sensitivity and Thermal analysis like Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

5.1 Noise level test

The noise level of FPSN was 107.9 dB (AI) and 131.6 dB(C) peak. The noise level for FPS5 was reduced by 13.0 % in dB (AI) and 9.65 % in dB(C) peak scale when compared to FPSN. Similarly, the noise level for FPS10 was reduced by 8.53 % in dB (AI) and 6.0 % in dB(C) peak scale when compared to FPSN. This showed that FPS10 was better and close to the noise level of FPSN when compared to FPS5.

5.2 Sensitivity Test

On comparing the sensitivity test, the limiting impact energy of the FPSN, FPS5 and FPS10 were 3.532 J, 3.532 J and 4.905 J and limiting frictional load was 324 N for FPSN and FPS5 and 360 N for FPS10. This implied that FPS10 was better in safety aspects during its handling. But, due to decrease in the sensitivity test by FPS10 there may be a chance for failure in cracking performance.

5.3 Thermal analysis

The thermal analysis revealed that better performance in noise level by FPS10 was due to the presence of volatile matter in TSP. More volume of gases was produced by 10 % of TSP in FPS10 than 5 % of TSP in FPS5 during devolatilization. This volatile matter in TSP decreased the thermal decomposition properties like onset, end and peak temperature along with ΔH and Ea. These properties improved the safety during handling and transportation of TSP based flash powders.

From TGA curve, onset temperature is found 226.43° C. The peak and end temperature were 270.75 and 281.06° C. The thermal decomposition is advances higher for FPS5 and FPN10.

The activation energy of the FPSN is 31.269 KJ/mol and heat dissipation rate (enthalpy) is 1440.48J/g. The increase in sulfur content is reducing the activation energy. But here even reducing the sulfur content by 5% and 10%, the activation energy is reduced. It is due to carbon derived from tamarind seed powder is balance sulfur role and enhancing the combustion efficiency. The heat dissipation rate of the FPS5 and FPS10 were 814.22 and 536.24 KJ/mol. It is greatly reduced than FPSN and increase the safety concern while using modified chemical composition.

5.4 Exhaust Gas Analyzer result

The emission rate of normal fire cracker is CO - 0.032, CO_2- 0.020, HC-15, O_2- 28.13, and SO_2 - 0.010. The emission rate of TSP based fire cracker (TSP5) is CO - 0.018, CO_2- 0.10, HC-6, O_2- 22.12, and SO_2 -0.008. The emission rate of TSP based fire cracker (TSP10) is CO - 0.016, CO_2- 0.12, HC-4, O_2- 21.12, and SO_2 - 0.007. The formation of CO is decreased when adding TSP to a chemical mixture and increase in the formation of CO_2 due to the presence of carbon content (47.76%) and Oxygen (42.39%) in TSP. The SO_2 level is gradually decreased for TSP based chemical mixture.

Chapter 6: Effect of Cashew Nut Shell Powder Based Fire Cracker for making Eco-Friendly Cracker

This chapter provides a study on emission analysis of tamarind based ground level pyrotechnic. Normally During bursting of fire cracker it discharge

the contaminated gases. In this chapter, the works are discussed regarding emission rate for normal fire cracker and modified fire cracker during bursting of the cracker and it is compared. The influence of modified fire cracker for the environmental pollution are also discussed.

6.1 Noise level test

On analyzing the noise level performance, all the pyrotechnic device were passed in the noise test by not exceeding the PESO standards. But the noise test values of CNSP5 pyrotechnic devices was close to SPFP devices and CNSP10 devices showed poor performance relative to SPFP and CNSP5.

6.2 Sensitivity Test

The limiting energy value of all the pyrotechnic formulation was 3.532 J indicating a sensitive chemical mixture to be handled with care and can be used in pyrotechnic devices. The friction load limit value for CNSP5 formulation was 360 N at which ignition occurs and was matching with the load limit of SPFP formulation. The ignition did not occur at 360 N for CNSP10 formulation confirming the chance of failure during the need for explosion.

6.3 Thermal Analysis

The mass loss % of CNSP5 and CNSP10 formulation was greater compared to SPFP ensuring better combustion than SPFP as confirmed by TGA analysis. The DSC analysis of all the pyrotechnic formulation concluded that the decomposition temperature of CNSP5 formulation was less with lower onset temperature relative to SPFP and CNSP10. In CNSP10 formulation, the decomposition temperature was increased compared to SPFP and CNSP5 due to more amount of lignin, a fire-retardant compound.

Based on above facts, the 5 % of CNSP was the optimized usage limit to be used in pyrotechnic formulation to reduce sulfur usage as confirmed by noise test, and safety and thermal analysis.

6.4 Exhaust Gas Analyzer result

The emission rate of CNSP based fire cracker (CNSP5) is CO - 0.027, CO_2- 0.20, HC-6, O_2- 31.36, and SO_2- 0.009. The emission rate of CNSP based fire cracker (CNSP10) is CO - 0.024, CO_2- 0.16, HC-4, O_2- 31.86, and SO_2- 0.008. The formation of CO is also decreased and increase in the formation of CO_2

when adding CNSP to a chemical mixture due to the presence of carbon content (45.21%) and Oxygen (37-47%) in CNSP. The SO_2 level also is decreased for CNSP based chemical mixture.

Chapter 7: Comparison of TSP and CNSP fire cracker

In this chapter compare the TSP and CNSP based fire cracker based on their behaviour. Based on the Noise level performance, TSP10 is gives more sound level than TSP5 and NFC. But, For CNSP5 noise level is closer to NFC. Its due to the presence of moisture content in CNSP may affect the noise level. Based on the impact sensitivity analysis, the limiting impact energy of TSP5 and NFC is 3.532J and it is slightly higher for TSP10 and it is 4.905J. Even though all the samples are under very sensitive category, the reactivity of TSP10 sample is slightly lesser due to reduction of sulfur powder in TSP10. Based on frictional test analysis, both TSP10 and CNSP10 poor reactivity and considering safety aspect is better. This fire cracker chemical mixture may fail when fabrication of cracker due to its chemical reaction.

Based on thermal analysis, the noise level of the TSP10 based fire cracker is better than TSP5 due to the presence of volatile matter in TSP and more volume of gases produced during devolatilization. On comparing CNSP based chemical mixture, the mass loss % of CNSP5 and CNSP10 formulation was greater compared to NFC ensuring better combustion than normal fire cracker chemical mixture. So, TSP10, CNSP5 and CNSP10 samples may better combustion due to its chemical reaction.

The rate of emission is reduced for TSP and CNSP-based fire crackers than a normal fire cracker. These TSP and CNSP- based fire cracker chemical mixture help to reduce the emission rate and make eco-friendly environment.

Overall aspect, TSP10 and CNSP5 samples are better for fabrication of bio mass based fire cracker than rest of the samples and its helps to improve the safety aspects and supports to reduce the environmental pollution.

Chapter 8: Conclusion

This chapter presents the summary of the current dissertation and conclusion of the research work. In addition, this chapter highlighting future scope of work.

Tamarind Seed Powder

- The noise level of the TSP based fire TSP10 sample closes to the normal fire cracker. For TSP5 sample, the noise level is slightly reduced due to produced less volume of gases when bursting. For TSP10 sample it is higher due to sudden expansion of more volume of gases produced by TSP during its decomposition reaction.
- The limiting impact energy of the TSP5 and normal fire cracker is 3.532 J. But for TSP10 sample it is increased from 3.532 J to 4.905 J. It is due to reduction of sulfur by 10% which causes to reduce the sensivitvy of the chemical mixture. The minimum 10% and maximum 17 % of sulfur is required to impart good cracking characteristics for the FPS and increased the limiting energy.
- The cracking performance of the TSP10 based chemical mixture may be failed due to the poor reactivity of the chemical mixture. This is due to 10% of sulfur only presented in this chemical mixture and this may affect the reactivity of the chemical mixture.
- The limiting frictional load for TSP10 is 360N. Even applying a maximum load of 360N over the chemical mixture, the flash does not occur. But, when considering the safety aspect, the TSP10 sample is better than the TSP5 sample. The safe frictional load for TSP5 and normal fire cracker is 324N. It is increased from 324N to 360N for TSP10-based chemical mixture.
- It is observed from thermal analysis, the noise level of the TSP10 based fire cracker is better than TSP5 due to the presence of volatile matter in TSP and more volume of gases produced during devolatilization. The rate of activation energy and heat dissipation rate is decreased for both TSP5 and TSP 10 samples than normal fire cracker chemical mixture.

Cashew Nut Shell Powder

- The noise level of the CNSP based fire cracker CNSP5 sample closes to the normal fire cracker. The limiting impact energy of the CNSP5, CNSP10 and

normal fire cracker chemical mixture is 3.532J. The reactivity of all chemical mixture is better for cracking characteristics.

- The frictional sensitivity test shows that, the sensivitvy of the CNSP10 based chemical mixture is poor due to its reactivity property. When considering safety aspect it is better than CNSP5 sample and considering the cracking behavior, CNSP 5 sample is better.
- Considering the thermal analysis, the mass loss % of CNSP5 and CNSP10 formulation was greater compared to SPFP ensuring better combustion than normal fire cracker chemical mixture. Thermal stability of the CNSP10 chemical mixture is higher than CNSP5 and normal fire cracker.
- The decomposition temperature closes to CNSP5 and normal fire cracker chemical mixture. It is increased for CNSP sample due to presence of fire retardant compounds. On comparing noise level, sensitivity of the chemical mixture, CNSP5 is better than CNSP10 sample. The both TSP and CNSP is better alternative fuel for fire cracker application and helps to make eco-friendly fire cracker.

Scope of the future work

- The study only focused on the importance of Tamarind Seed Powder and Cashew Nut Shell powder for making the environment free fire cracker.
- The other fuel also to be introduce for making eco-friendly fire cracker and it is compare with Tamarind Seed Powder and Cashew Nut Shell powder.

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